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(54) HEAT-SHRINKABLE POLYOLEFIN RESIN FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a heat-shrinkable polyolefin resin film satisfying low temperature shrink characteristic and transparency.

SOLUTION: In the film constituted of polyolefin resin, polyolefin resin is a polypropylene-1-butene random copolymer where the content of 1-buten unit is in the range of 5 to 50 mol%.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention is excellent in transparency and low-temperature shrinkage characteristics, and relates to the film for polypropylene system shrink labels in which PET and judgment are possible by a specific gravity method.

[0002]

[Description of the Prior Art]In recent years, the shrink label is widely used protection of the package for avoiding the shock of the exterior and contents directly, a tight package, a glass bottle, or a plastic bottle, and for the purpose of the label package etc. which served as the display of goods for the improvement in appearance of packaging goods. Gravure printing of the printing is carried out in many cases, and seven or more colors may usually be printed in three to 5 color. since a printing surface turns into a label inner surface and a printing surface will be seen through a film, when it becomes a final product (label) -- Hayes - - it is high (opaque) -- it becomes a problem.

[0003]If inferior to low-temperature shrinkage characteristics, when the label set to the bottle will finish through a shrink tunnel, it does not fit firmly, but result nonuniformity is seen, and it becomes a problem.

[0004]As a plastic material used for these purposes, polyvinyl chloride, polystyrene, polyethylene terephthalate, polyolefine, etc. are known. However, although the polyvinyl chloride label is excellent in the shrink characteristic, it generates gaseous chlorine at the time of incineration, and has problems, such as environmental pollution. Although heat contraction nature is good about polystyrene and a polyethylene terephthalate label, since specific gravity with a polyethylene terephthalate bottle is ****, floating separation becomes difficult and bars the recycling efficiency of a polyethylene terephthalate bottle. Since bad heat-resistant polymer is used in order to obtain sufficient heat contraction nature, if retort sterilization is performed, the printer's ink flow by melting polymer will be produced.

[0005]Also in a polyolefin system, the film of repro pyrene can do extension easily, although the film is a film with good transparency, since heat-sealing temperature is high, a result in which low-temperature shrinkage characteristics are inferior is brought, and there is a big fault as a business-use wrap film or a shrink package wearing film.

[0006]as the policy which solves these faults -- ethylene -- about 3-5wt% -- the propylene-ethylene random copolymer which carried out copolymerization. ethylene -- 1 - 3wt% and 1 **BUTEN -- about 3-10wt% -- although there is a film by which biaxial stretching treatment was carried out in the propylene-ethylene-1

**BUTEN random copolymer of 3 yuan which carried out copolymerization, and transparence and gloss are excellent, it has the fault of being inferior to low-temperature shrinkage characteristics. If it passes through the amount of copolymerization and is made to increase in order to raise low-temperature shrinkage characteristics, it will result in it being inferior in transparency.

[0007]Otherwise, the multilayer shrink film which used the propylene-ethylenic copolymer as both the epidermis layer is known by using linear polyethylene resin as a core layer. According to the knowledge of (JP,58-166049,A public relations), however this invention persons. surely, have an advantage of the both sides of linear polyethylene resin and a propylene-ethylenic copolymer, and transparence and gloss are excellent -- the ****-proof characteristic -- being certain -- although grade improvement was carried out, about low-temperature shrinkage characteristics, it was insufficient.

[0008]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to be able to satisfy low-temperature shrinkage characteristics and transparency, and to provide the polypropylene film for shrink labels in which PET and judgment are possible by a specific gravity method.

[0009]

[Means for Solving the Problem]Then, this invention persons came to complete this invention at last, as a result of trying hard and inquiring and studying wholeheartedly transparency and low-temperature shrinkage characteristics which are aforementioned problems that it should improve. Namely, a heat contraction nature polyolefin-system-resin film of the invention in this application, It is a film which consists of polyolefin system resin, and said polyolefin system resin is characterized by being a propylene-of as [whose content of 1 **BUTEN unit is 5-50 mol% of the range] 1 **BUTEN random copolymer.

[0010]In this case, it is preferred that specific gravity of said heat contraction nature polyolefin-system-resin film is 1.0 or less.

[0011]It is preferred that Hayes after heat treatment of said heat contraction nature polyolefin-system-resin film is 8% or less, and a heat shrinkage rate is not less than 30% in this case.

[0012]

[Embodiment of the Invention]The heat contraction nature polyolefin-system-resin film of this invention comprises a monolayer or lamination.

[0013]Resin in this invention comprises a propylene-1-butene random copolymer preferably, although what consists of propylene homopolymers, and the thing which carried out copolymerization of ethylene, the butene, etc. to propylene are raised.

[0014]1-butene is used for a propylene-1 **BUTEN random copolymer as comonomer -- the content of 1 **BUTEN unit -- 5-50-mol % -- it is 10-40-mol % preferably. Since low-temperature shrinkage characteristics are not revealed at less than 5 mol %, and a film will produce blocking or butene content will produce natural contraction at the time of storage if it is more than 50 mol %, there is no ** diminished to practical use.

[0015]One **BUTEN unit is measured from the characteristic absorption of 770 cm^{-1} using an infrared spectrophotometer. About the propylene-1 **BUTEN random copolymer, the measurement by an infrared spectrophotometer produced the analytical curve with the fixed-quantity value by C-NMR, and quantified. The cold xylene fusible part (CXS) of a propylene-1-butene random copolymer is 2 to 50 % of the weight

more preferably one to 60% of the weight.

[0016]the melt flow rate (MFR) of the above-mentioned copolymer -- usually -- 5-15g/-- they are 4-10g/10 minutes preferably for 10 minutes. 100-150 ** of melting points of the above-mentioned copolymer are usually 110-140 ** preferably.

[0017]About 10-mg test piece cut down from the sheet with a thickness of 0.5 mm which specifically produced the melting point with heat pressing is put into the sample for DSC measurement, and after carrying out preheating, lowering the temperature to ordinary temperature and holding for 5 minutes at 230 **, temperature up is carried out the speed for 5 **/, and it is quantified and measured from the thermograph.

[0018]What is called Ziegler-Natta catalyst, i.e., the 4-8th group transition metal compound of the periodic table, and the organic compound of the 1-3rd fellows type metal of the periodic table which are the catalysts for the stereospecific polymerization of alpha olefin with the above-mentioned copolymer publicly known as a catalyst system, for example, It can obtain by polymerizing using what consists of a third component of an electron donor compound preferably.

[0019]The gas phase polymerization process etc. which polymerize as a polymerizing method in the solvent polymerizing method which polymerizes in a solvent, or the gaseous phase are mentioned.

[0020]The method in particular of obtaining the above-mentioned resin composition is not limited, and publicly known arbitrary methods, for example, the extrusion melting blending method, the Banbury blending method, etc. are mentioned. The film in this invention is a range which does not check this invention, and, for example, may make additive agents, such as a spray for preventing static electricity, a blocking-proof agent, lubricant, a **** agent, stabilizer, and a nucleating agent, contain.

[0021]The heat contraction nature polyolefin-system-resin film of this invention is obtained by extending the sheet fabricated by T pressure die casting which used the dice, for example with publicly known extension methods, such as the tenter method or roll extension, to at least 1 shaft orientations, for example, a TD direction, or MD directions.

[0022]If the heat contraction nature polyolefin-system-resin film of this invention is not extended by at least 1 shaft orientations, it will become poor in the finished surface of a container package. In order to obtain a film with good low-temperature shrinkage characteristics especially, it is necessary to carry out orientation of the film enough by extension.

[0023]For that purpose, the extension temperature of a film is with a very important element. A temperature lower 10 ** than the melting point of resin and the oriented film where a film carries out orientation enough and which has good low-temperature shrinkage characteristics when it extends preferably in a not less than 40 ** temperature requirement are obtained from the extension temperature of 40 **.

[0024]however, as a result of examining extension conditions and a heat treatment condition from balance with transparency, it becomes possible by changing extension temperature, draw magnification, and a stretching speed to be compatible in low-temperature shrinkage characteristics and transparency -- the draw magnification is four to nine preferably. In this invention, a heat shrinkage rate is not less than 40% preferably not less than 30%. At less than 30%, it is inferior to a label moldability.

[0025]In this invention, Hayes after heat treatment is 5% or less preferably 8% or less. If 8% is exceeded, printing is not in sight easily.

[0026]

[Example] Hereafter, although this invention is explained based on an example, this invention is not limited to these examples. The data and evaluation in an example and a comparative example were performed in accordance with the following method.

[0027] (1) The size before and behind heating of MD directions (extension and rectangular directions) when a sample with a heat shrinkage rate length of 100 mm x 100 mm is immersed in 90 °C warm water for 10 seconds, or a TD direction (the extension direction) was measured, and heat shrinkage was computed based on the following formula.

It measured based on heat shrinkage (%) = (size after front [heating] size - heating) / (front [/heating] size) x 100 [JIS Z 1709].

[0028] (2) It heat-treated in Hayes 90 °C x 10 second, and measured using Nippon Denshoku Industries Co., Ltd. make hazemeter NDH1001DP based on JIS K 7105.

[0029] (3) It measured using the outside heat type DSC which used PTC-10A of the product thermostat flex time series made from Melting point Physical science Electrical and electric equipment of polymer as the temperature controller.

[0030] (4) It measured based on MFR [JIS K7210].

[0031] (5) The quantity 1 g BUTEN unit of the butene measured using the infrared spectrophotometer (FTIR-8100M/Shimadzu).

[0032] (Example 1) a propylene-1-butene random copolymer (the Sumitomo Chemical Co., Ltd. make.) 27 mol of content % and the melting point of 130 °C of Sumitomo no BUREN and 1-butene unit, and the resin composition containing part 100 % of the weight for melt flow rate 5g/were extruded from the T die at 220 °C, and it twisted around a 15 °C cooling drum, and quenched, and the unextended sheet was produced. After heating this sheet at 50 °C, it extended 6 times to the TD direction at 60 °C, and further, the stretching speed was carried out by a part for 2000%, and obtained the 60-micrometer-thick horizontal uniaxial-stretching shrink label film. By heat-treating the obtained film for 10 seconds at 90 °C, the heat shrinkage rate was acquired [Hayes] for the good label of low-temperature shrinkage characteristics and transparency by 4.8% in 5% of the lengthwise direction, and 42% of the transverse direction.

[0033] (Comparative example 1) a propylene-ethylene-1-butene random copolymer (the Sumitomo Chemical Co., Ltd. make.) Sumitomo no BUREN, 2.1 % of the weight of content of an ethylene unit, 5.7 % of the weight of content of 1-butene unit, The melting point of 138 °C and the resin composition containing part 100 % of the weight for melt flow rate 5g/were extruded from the T die at 240 °C, and it twisted around a 15 °C cooling drum, and quenched, and the unextended sheet was produced. After heating this sheet at 80 °C, at 40-80 °C, at 90 °C extended to a TD direction, and no temperature, a film was not able to fracture and it was able to extend.

[0034]

[Effect of the Invention] The film of this invention has good low-temperature shrinkage characteristics, and the heat contraction nature polyolefin-system-resin film which is excellent in transparency can be provided. Since there is also no environmental problem like polyvinyl chloride, the heat contraction nature polyolefin-system-resin film of this invention is preferred. Since specific gravity is 1.0 or less, floating separation with a polyethylene terephthalate bottle is performed simply, and recycling efficiency is raised.

[Translation done.]